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Synthesis of nopol over MCM-41 catalysts

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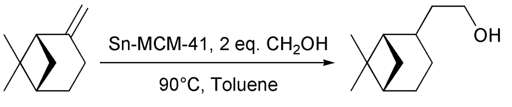
MCM-41 was found to be an active heterogeneous catalyst for the synthesis of nopol by the Prins condensation of β-pinene and paraformaldehyde, but Sn-MCM-41 in which Sn has been grafted on MCM-41 by chemical vapor deposition is far more active and combines high efficiency and recyclability.

Recently, special emphasis has been placed on using natural renewable raw materials to obtain higher value added products. In this sense terpenes are widely employed to produce a wide variety of products such as aromas, food additives, agrochemicals and pharmaceuticals. Among terpenes α- and β-pinenes are the major components of wood turpentine and of numerous other volatile oils. β-Pinene is a precursor of nopol, an optically active bicyclic primary alcohol, useful in the agrochemical industry to produce pesticides. It is also used in the preparation of soap perfumes, and household products.[1] Three general methods have been used to obtain nopol:[2] (1) β-pinene and paraformaldehyde in acetic acid solution at 120 °C yields nopyl acetate which is saponified to nopol; (2) heating a mixture of β-pinene and paraformaldehyde in the presence of a small quantity of a homogeneous catalyst such as zinc chloride at 115–120 °C for several hours yields about 57% nopol. In both methods monocyclic isomers and other side products are formed; (3) autoclaving paraformaldehyde and β-pinene at 150–230°C for several hours yields quantitative amounts of pure nopol.

In recent years, environmental and economic considerations have promoted process innovation toward cleaner technologies. Therefore, there is a great challenge to use heterogeneous catalysts that can perform under milder reaction conditions, *i.e.* lower temperatures, pressures, and which avoid the use of noxious substances and the generation of toxic waste. Recently, a MCM-41 anchored quaternary ammonium chloride/$SnCl_4$ catalyst was reported for the Prins condensation of isobutene and formaldehyde to isoprenol.[3] Yields of 90% alcohol were obtained at 60 °C during 3.5 h. However, catalyst preparation involved several steps and no report on the activity of the MCM-41 support was given. Besides, the reaction was carried out in the presence of a chlorinated solvent. We here report our preliminary results on the heterogeneous catalytic synthesis of nopol from β-pinene and paraformaldehyde over MCM-41 and Sn grafted MCM-41 by CVD (Scheme 1). The latter catalyst required no solvents or vacuum during its preparation. Furthermore, high yields of nopol were obtained without the use of chlorinated solvents.

MCM-41 was synthesized according to the procedure reported by Grun,[4] with cethyltrimethylammonium bromide (CTABr) as template. The molar gel composition was TEOS : 0.15 CTABr : 2.8 NH_3 : 141 H_2O. The XRD pattern for the as-synthesized sample exhibits a strong [100] reflection peak with two small peaks, characteristic of MCM-41 material. After the organic template was removed by calcination,† the intensity of the [100] diffraction slightly increased while the peak position shifted to the low-angle region as previously observed.[5] The BET surface area is 1202 $m^2\ g^{-1}$ and the pore diameter 1.98 nm. To obtain Sn grafted MCM-41, 1.0 g of MCM-41 was exposed to the vapor produced by 1.0 ml $SnCl_4$ (Aldrich) at 100 °C in a Teflon-lined SS autoclave under autogenous pressure. After about 8 h the sample was removed from the autoclave, thoroughly washed with deionized water and calcined to remove the organic template.† The resulting material, Sn-MCM-41, exhibited little decrease in the N_2 adsorption capacity and pore diameter. Besides, the MCM-41 structure remained intact after the Sn deposition. The amount of chlorine present in Sn-MCM-41 as determined by ionic chromatography was 2.13 mmol g^{-1} and the Sn content obtained by atomic absorption was 0.51 mmol g^{-1}. The tin/chlorine atomic ratio in the fresh catalyst was found to be 0.24 which is close to that in $SnCl_4$. The UV-VIS diffuse reflectance spectra of calcined Sn-MCM-41 samples reveal an absorption band at about 208 nm. This band has been assigned[6] to the presence of isolated Sn^{4+} in tetrahedral coordination.

MCM-41 and Sn-MCM-41 were used to catalyze the Prins condensation of β-pinene and paraformaldehyde under stirring at 90 °C in the presence of toluene as solvent. For comparison



Scheme 1 Prins condensation of β-pinene and formaldehyde to nopol.

Table 1 Condensation of β-pinene and formaldehyde to nopol over silica based catalysts and catalyst recycling[a]

Entry	Catalyst	$SnCl_4$ loading/ mmol (g support)$^{-1}$	Conversion of β-pinene (%)	Nopol selectivity (%)
1	Silica gel[b]	—	37.1	96.1
2	MCM-41[b]	—	61.3	98.7
3	Recycling 1[c]	—	40	98.7
4	Sn-MCM-41	0.51	98.9	80.5
5	Recycling 1[d]	0.51	99.8	93.5
6	Recycling 2[d]	0.50	99.3	93.9
7	Recycling 3[d]	0.50	99.6	98
8	Sn-MCM-41[e]	0.51	60	65

[a] Procedure: 0.5 mmol of β-pinene, 1 mmol paraformaldehyde, catalyst containing 12 μmol of Sn and 1 mL of toluene were introduced into a glass reactor and stirred for 6.5 h at 90°C. [b] 100 mg catalyst. [c] Recycling of MCM-41. [d] Recycling of Sn-MCM-41 after exhaustive washing with acetone at 40 °C and drying at 100 °C. [e] Reaction temperature 55 °C, reaction time 2 h.

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purposes we also tested silica gel (J. T. Baker; average pore diameter, 15 nm). The catalytic results together with the $SnCl_4$ catalyst loadings in mmol (g support)$^{-1}$ are summarized in Table 1.

From Table 1 it is clear that MCM-41 and silica gel are active and selective for nopol production, though MCM-41 is more active than silica gel. The accessibility of the reactants to the active sites in the regular and well ordered hexagonal array of MCM-41 pores allows better diffusion of bulky reactants and products as compared to silica gel.

However, after reusing MCM-41 its activity decreases and the catalyst needs to be regenerated by calcination.† In contrast, Sn-MCM-41 is an excellent catalyst for the Prins condensation of β-pinene and paraformaldehyde to nopol. It can be reused after washing with acetone at 40 °C and drying at 100 °C. No loss of activity was observed after 5 runs. Instead, its selectivity increases with recycling. We verified that the reaction does not occur in the absence of catalyst and it is not the result of homogeneous catalysis by leached elements. The solid catalyst was filtered out at the reaction temperature, just after 5 min reaction when β-pinene conversion was only about 5%. This stopped the reaction with no further conversion being observed within the next 24 h. Furthermore, as can be observed in Table 1, elemental analysis of Sn in recycled samples confirms that Sn-MCM-41 is resistant to leaching under the reaction conditions used. The Sn-MCM-41 activity and selectivity to nopol increase with the reaction temperature from 25 °C up to 90 °C. As shown in Fig. 1, the reaction is much faster over Sn-MCM-41 that on MCM-41.

The present results confirm the previous finding[3] that Sn(IV) cations immobilized on MCM-41 material using $SnCl_4$ precursor are efficient catalytic sites for Prins condensation not only of simple unsaturated olefins but also of a complex molecule containing double bonds, such as nopol. Preliminary characterization results suggest that CVD of $SnCl_4$ lead to a uniform distribution of the volatile complex throughout the mesoporous structure of MCM-41 without cluster formation. The new Sn-MCM-41 catalyst is an efficient, selective and recyclable catalyst to for the production of nopol by the Prins condensation of β-pinene with paraformaldehyde in the presence of toluene. Thus, efficient Sn(IV) sites can be created by a simplified CVD method and the highly selective and recyclable catalyst does not need a chlorinated solvent.

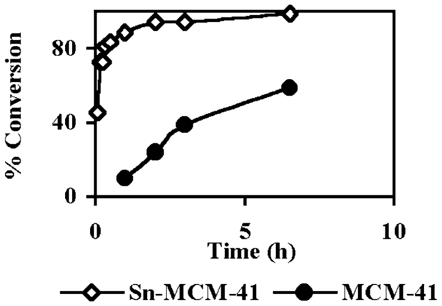

Fig. 1 Conversion of β-pinene *vs.* time on MCM-41 and Sn-MCM-41. Reaction conditions: 0.5 mmol of β-pinene, 1 mmol paraformaldehyde, 100 mg catalyst, 90 °C.

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Notes and references

† Calcination was performed by heating the dried solid at 1 °C min^{-1} to 550 °C and holding this temperature for 5 h.

1 *Common Fragance and Flavor Materials. Preparation, Properties and Uses*, ed. K. Bauer, D. Garbe and H. Surburg, VCH Verlagsgesellschaft, Weinheim, 1990, p. 59.
2 J. P. Bain, *J. Am. Chem. Soc.*, 1946, **68**, 638.
3 T. M. Jyothi, M. L. Kaliya, M. Herskowitz and M. V. Landau, *Chem. Commun.*, 2001, 992.
4 M. Grun, *Microporous Mesoporous Mater.*, 1999, **27**, 207.
5 L. Nikiel and T. W. Zerda, *J. Phys. Chem.*, 1991, **995**, 4063.
6 K. Chaundhari, T. K. Das, P. R. Rajmohanan, K. Lazar, S. Sivasanker and A. J. Chandwadkar, *J. Catal.*, 1999, **183**, 281.